Molecular Simulation Research Projects

Introduction to Molecular Dynamics

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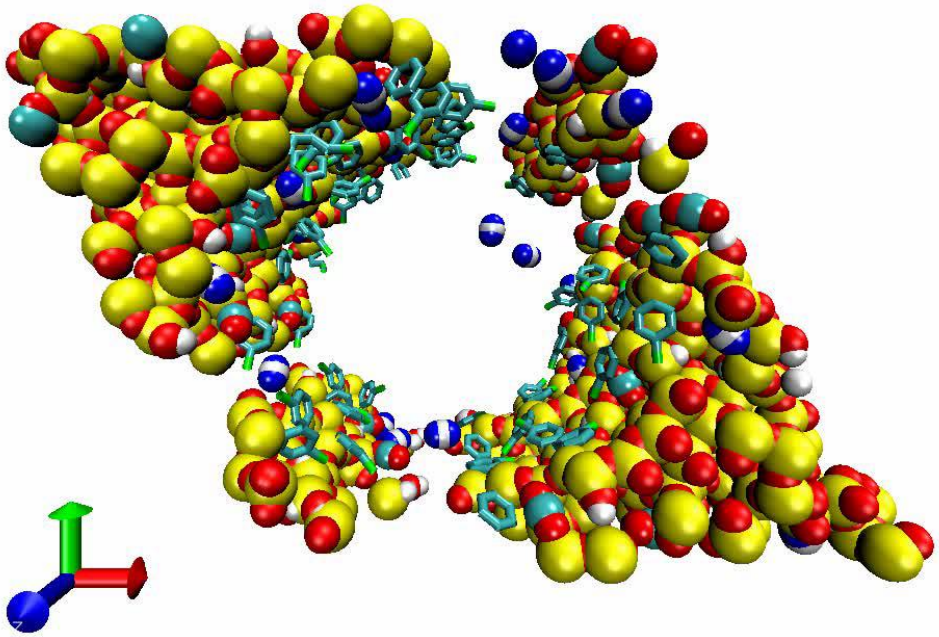
Molecular Dynamics is easy (in principle)

$$\mathbf{F} = m\frac{d^2\mathbf{r}}{dt^2}$$

- Compute the forces on acting on a particle
- Integrate Newton's equation of motion to get trajectories
- Sample for desired properties every now and then.

An example

Finding optimal surface groups for CO_2 capture applications

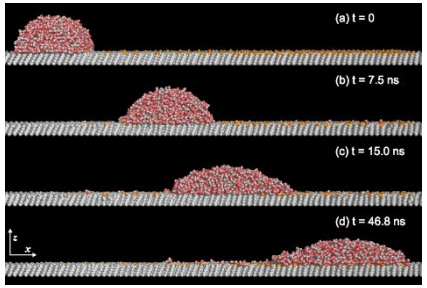


Jennifer Williams, Tina Düren

What else is MD used for?

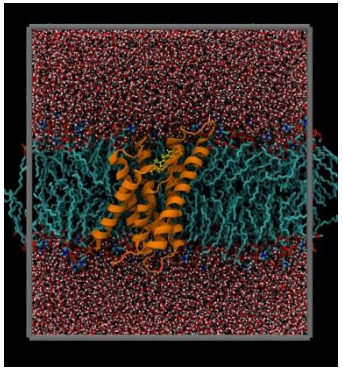
- Materials property prediction
  e.g. bulk modulus, surface tension, shear viscosity, thermal conductivity
- Biomolecular modelling
  e.g. protein folding, cell membranes, ion transport
- Ligand and drug design
  e.g. docking, interaction, sterics
- High-throughput molecular screening
  e.g. drugs, surfactants, self-assembling materials

Wetting



http://lisgi1.engr.ccny.cuny.edu/jkres.htm

Protein in lipid bilayer

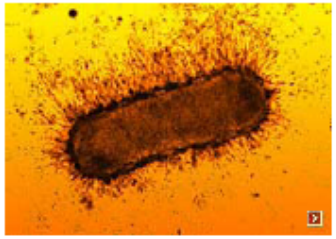


http://www.molecular-simulation.org/thit.html

What length scales are we dealing with?

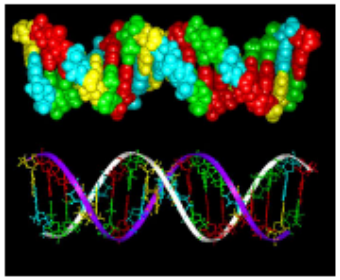
Macroscale

- Time > 1 *s*
- Lengthscale > 1 μ
- Phase field models, FEM



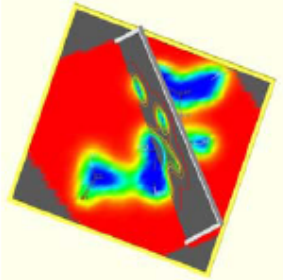
Mesoscale

- Time ~ $10^{-8} - 10^{-2}$ *s*
- Lengthscale ~ 10-1000 nm
- DPD, coarse-graining



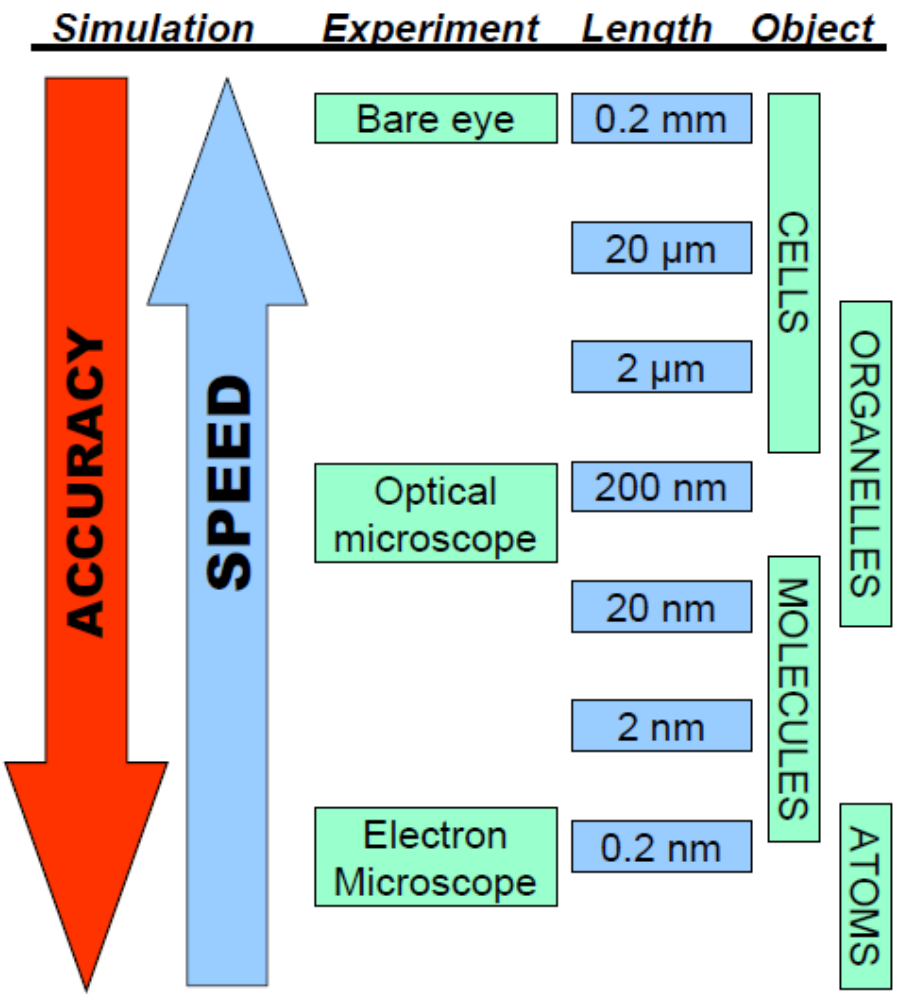
Nanoscale

- Time ~ $10^{-15} - 10^{-9}$ *s*
- Lengthscale ~ 0.1 - 10 nm
- Molecular dynamics, Monte Carlo



Subatomic scale

- Electronic structures
- *Ab initio*

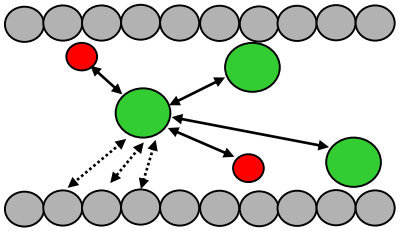


http://reaktiveplasmen.rub.de/files/lehre/md/01-1.pdf

What is Molecular Dynamics?

- In MD, we model the motion of some group of particles (e.g., atoms) by solving the classical equations of motion.

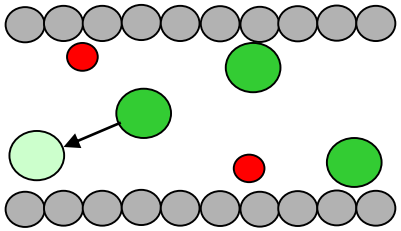
1. Calculate the force acting on a molecule



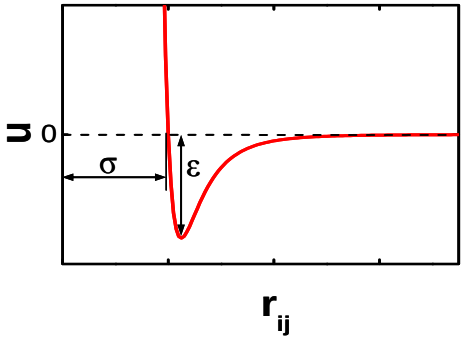
$$\frac{d^2\mathbf{r}_i(t)}{dt^2} = \frac{1}{m_i}\mathbf{f}_i(t)$$

$$= -\frac{1}{m_i}\frac{\partial U\left(\mathbf{r}^N\right)}{\partial \mathbf{r}_i}$$

2. Integrate Newton's equations of motion to get new position



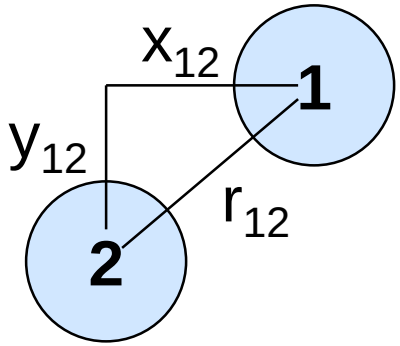
Remember: e.g. Lennard Jones potential to describe interaction between two particles



$$u(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

Force calculations

- Force is the gradient of the potential



$$\mathbf{F}_{2\to 1} = -\nabla u(r_{12})$$

Force on 1, due to 2

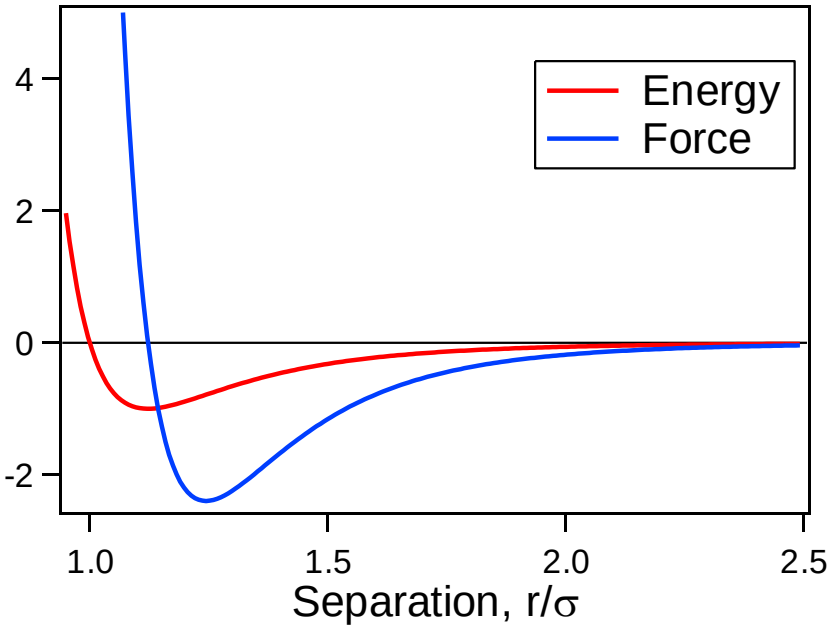
$$= -\frac{\partial u(r_{12})}{\partial x_1}\mathbf{e}_x - \frac{\partial u(r_{12})}{\partial y_1}\mathbf{e}_y$$

$$= -\frac{du(r_{12})}{dr_{12}}\left[\frac{\partial r_{12}}{\partial x_1}\mathbf{e}_x + \frac{\partial r_{12}}{\partial y_1}\mathbf{e}_y\right]$$

$$= -\frac{f(r_{12})}{r_{12}}\left[x_{12}\mathbf{e}_x + y_{12}\mathbf{e}_y\right]$$

$$r_{12} = \left[(x_2 - x_1)^2 + (y_2 - y_1)^2\right]$$

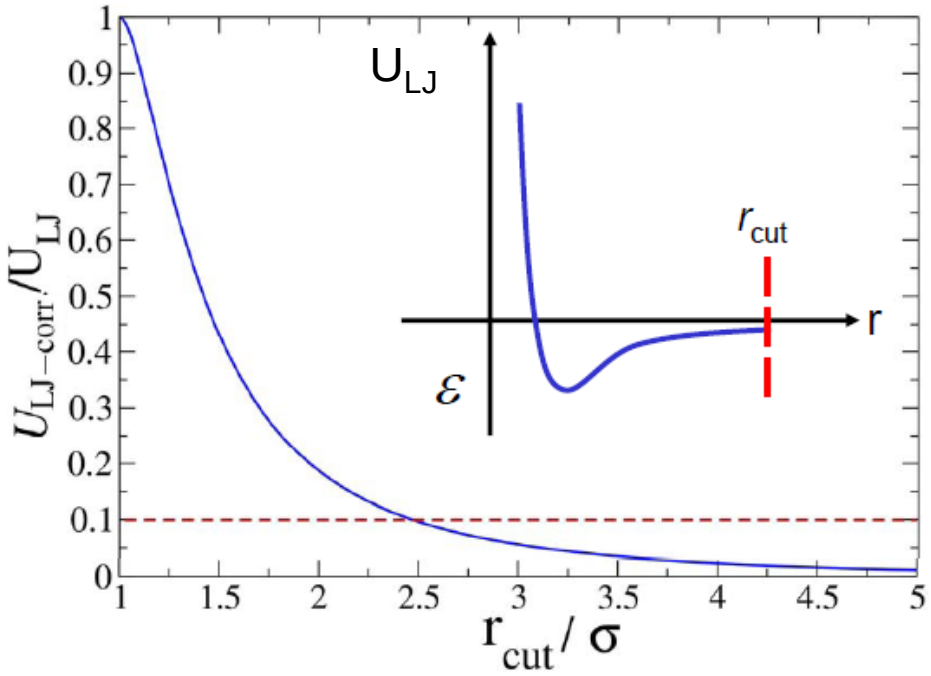
$$\mathbf{F}_{2\to 1} = -\mathbf{F}_{1\to 2}$$



Cutting off the potential

- For an N particle system, we need to perform N(N-1)/2 force calculations.
- Luckily, most potentials are (relatively) short ranged and contributions from particles that are further away can be neglected.
- Consider interactions only if particles are closer than some cut-off radius r_{cut}.
- The error can be made arbitrarily small by choosing a large cut-off radius.

Truncation error
At 2.5·σ error in energy is ~10 %



U_{LJ}: Lennard Jones potential truncated at r_{cut}.

$U_{LJ\text{-}corr}$: truncated Lennard Jones potential corrected with tail correction

- Can I live with that?
- Increase the cut-off radius?
- Use tail corrections?

} Increase in computational effort

} Depends on application

http://reaktiveplasmen.rub.de/files/lehre/md/02-2.pdf

Ways to truncate the potential

- Simple truncation = ignore all interactions beyond r_{cut}

$$u^{trunc}(r) = \begin{cases} u^{LJ}(r) & r \le r_{cut} \\ 0 & r > r_{cut} \end{cases}$$

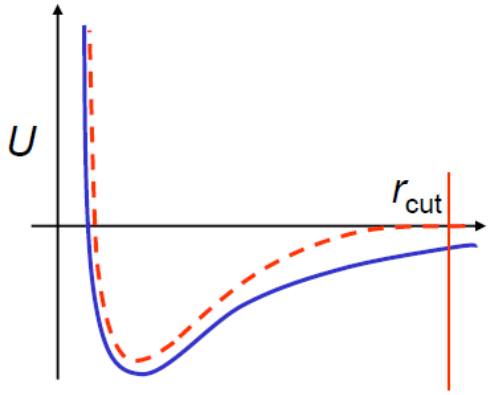
- Very often used for Monte Carlo simulations.

- Unsuitable for MD simulations as potential changes discontinuously at r_{cut} . This will result in an infinite force at the discontinuity.

Truncated and shifted potential

- The potential is truncated and shifted such that the potential vanishes at the cut-off radius

$$u^{tr-sh}(r) = \begin{cases} u^{LJ}(r) - u^{LJ}(r_{cut}) & r \le r_{cut} \\ 0 & r > r_{cut} \end{cases}$$



- Most commonly used approach in MD.

Integrating the equations of motion

- Desirable features of an integrator
  - minimal need to compute forces (a very expensive calculation)
  - good stability for (relatively) large time steps
  - good accuracy
  - conserves energy and momentum

Verlet algorithm

- Very simple, very good, very popular algorithm
- Consider expansion of coordinate forward and backward in time

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{\mathbf{f}_i(t)}{2m_i}\Delta t^2 + \frac{\dddot{\mathbf{r}}_i(t)}{3!}\Delta t^3 + O(\Delta t^4)$$

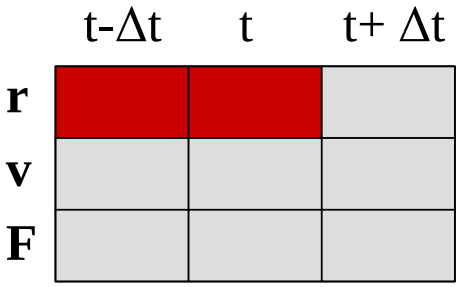
$$\mathbf{r}_i(t-\Delta t) = \mathbf{r}_i(t) - \mathbf{v}_i(t)\Delta t + \frac{\mathbf{f}_i(t)}{2m_i}\Delta t^2 - \frac{\dddot{\mathbf{r}}_i(t)}{3!}\Delta t^3 + O(\Delta t^4)$$

- Which results in

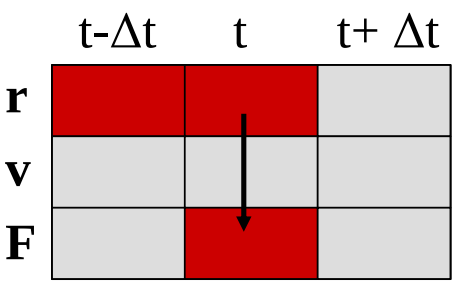
$$\mathbf{r}_i(t+\Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t-\Delta t) + \frac{\mathbf{f}_i(t)}{m}\Delta t^2 + O(\Delta t^4)$$

Verlet algorithm illustrated

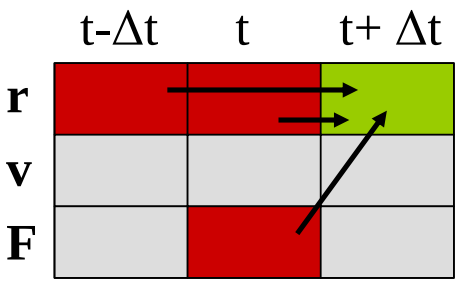
$$\mathbf{r}_i(t+\Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t-\Delta t) + \frac{\mathbf{f}_i(t)}{m}\Delta t^2 + O(\Delta t^4)$$



current position and position at end of previous time step known



Use them to compute the force at the current position



Use all three to compute the new position, repeat

- Calculation of new position without consulting velocity
- Velocities can be calculated from finite difference

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t+\Delta t) - \mathbf{r}_i(t-\Delta t)}{2\Delta t} + O(\Delta t^2)$$

- Biggest disadvantage: Calculated velocities lag behind by one time step

Schematic from Allen & Tildesley, Computer Simulation of Liquids

Large time steps lead to energy drifts

- For any time step, numerical errors that accumulate result in long-term “energy drift” – an exponential increase in energy for very large number of integration steps.
- Typically, $\Delta t^* = 0.005$ required for stability

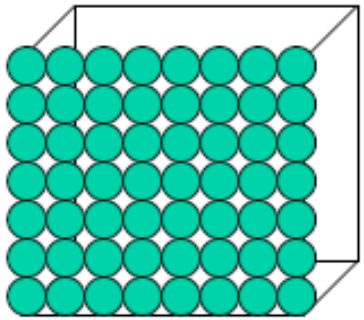
$$t^* = \frac{t}{\sigma\sqrt{\varepsilon / m}}$$

  - For argon limit of stability $\Delta t = 10$ fs (1 fs $=10^{-15}$ s)
  - For more complex systems, $\Delta t = 1 – 2$ fs

More advanced integration schemes

- Leapfrog (default in gromacs)
- Velocity Verlet
- Predictor / Corrector methods

Boundary effects



- In small systems, boundary effects are always large.
- 1000 atoms in a simple cubic crystal: 488 boundary atoms.
- 1,000,000 atoms in a simple cubic crystal: still 6% boundary atoms…

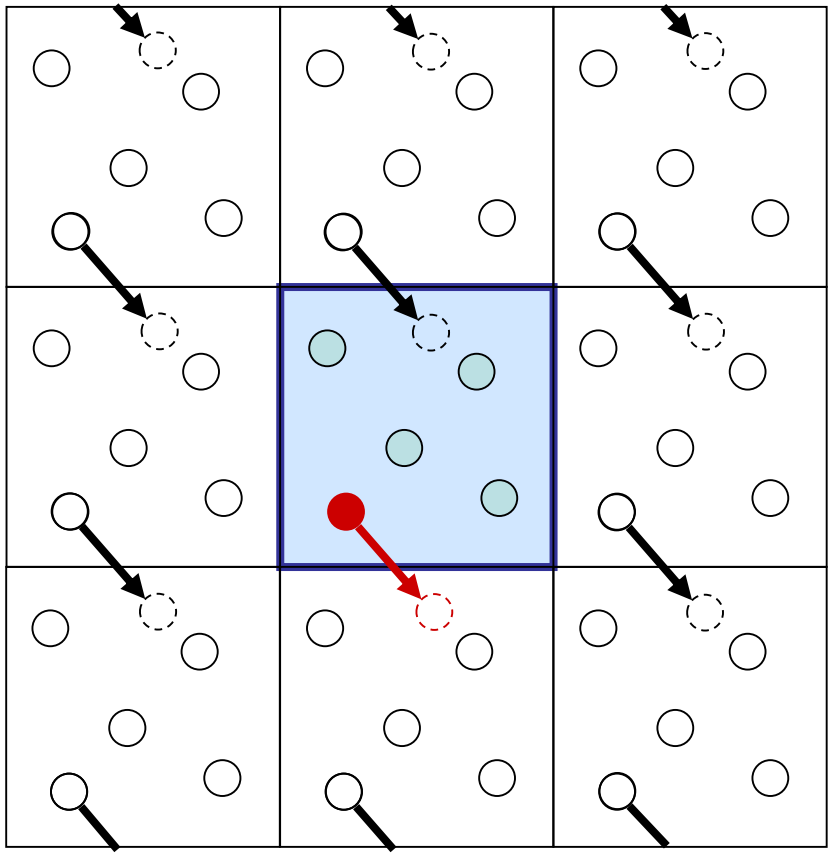
How can we handle limited system size?

- We try to get information about the macroscopic system.
- But due to computational limitations we can only handle system sizes of a few nm.
- This could lead to severe boundary effects.
- We have to find boundary conditions that mimic the infinite bulk surrounding our model system.

➡ Periodic boundary conditions

Periodic boundary conditions

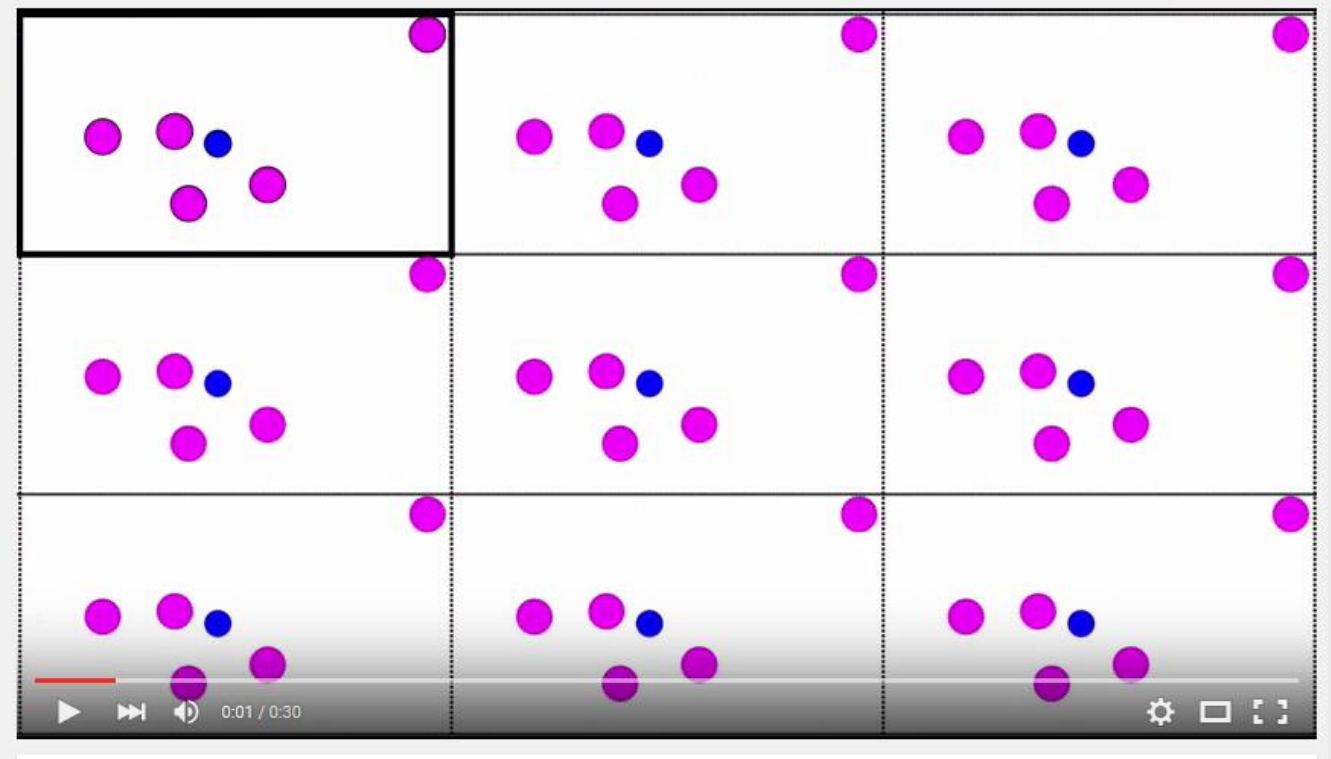
Central box surrounded by its eight images in 2D (26 in 3D) to mimic infinite bulk phase



If a particle leaves the central cell, an image particle enters from an adjacent cell.

Simulation box: simulation with five particles

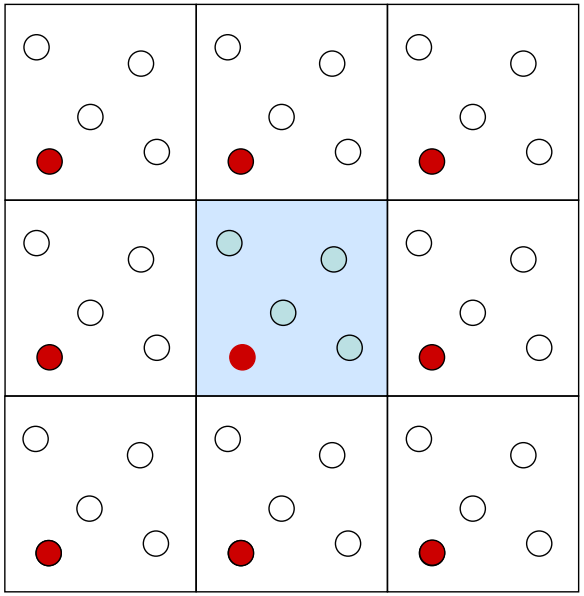
Demonstration of pbc



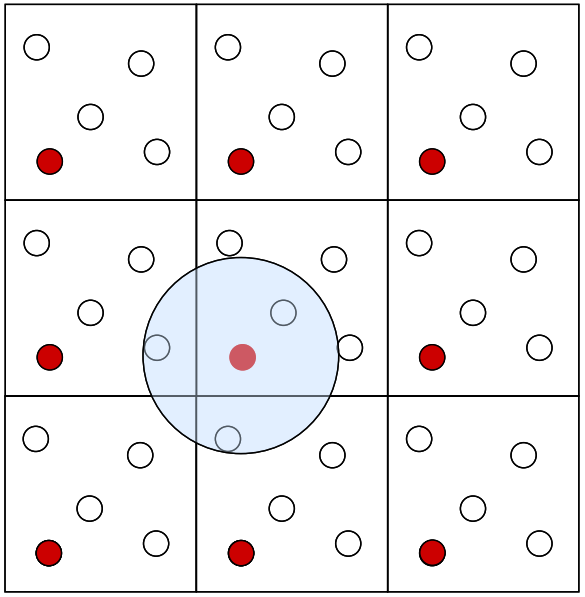
- https://www.youtube.com/watch?v=5qdNafdyaG0
- Better as interactive: http://www.eng.buffalo.edu/~kofke/applets/dak_pbcCubic.html (you will have to add http://www.eng.buffalo.edu as a trusted site to java)

Minimum image convention

- We have to avoid that a molecule is interacting with itself.

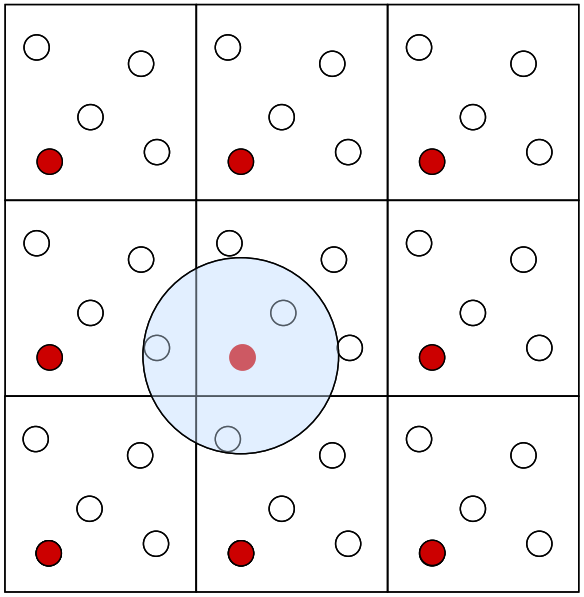


All the red particles are the same.



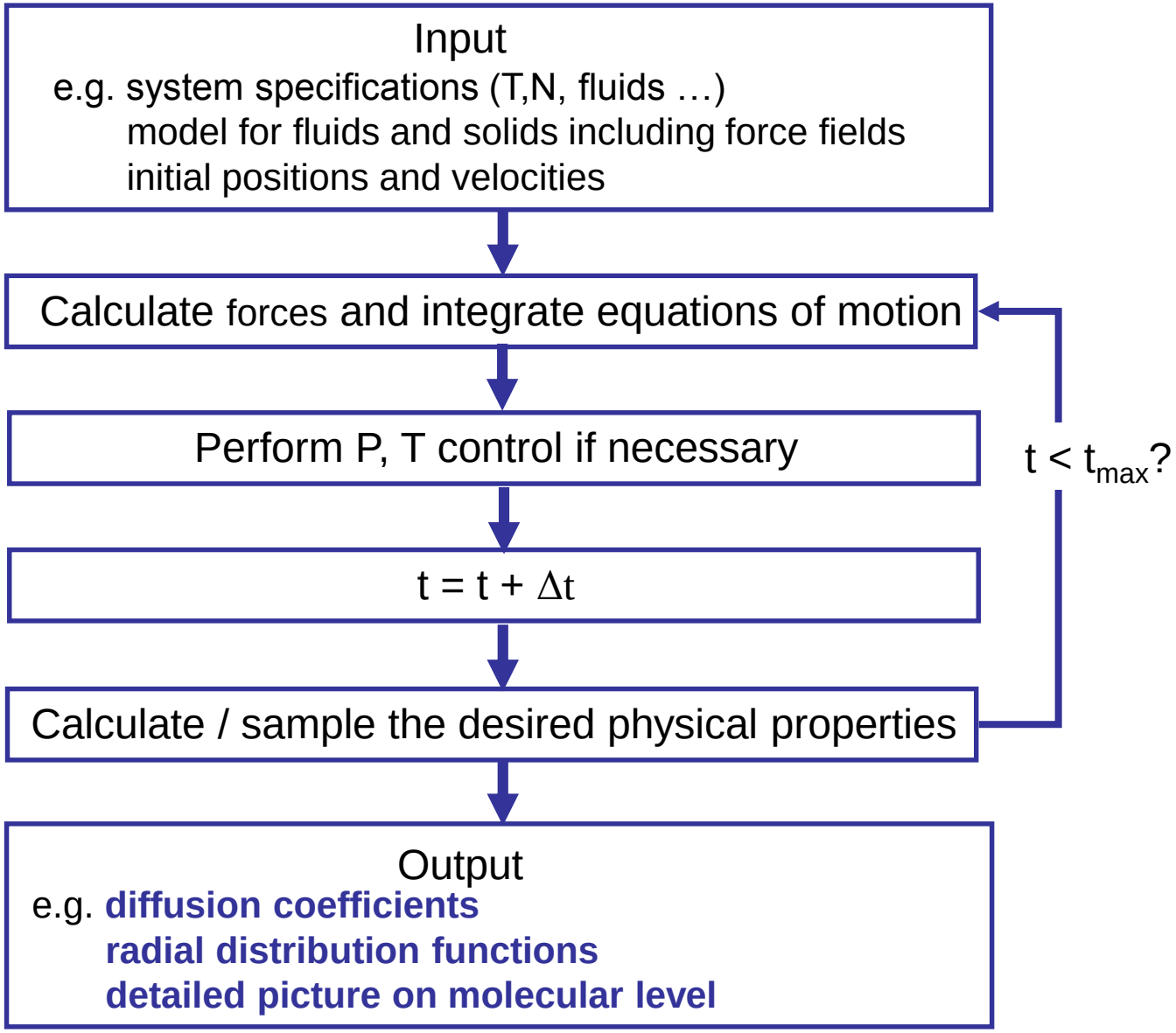
Interactions are only considered with the closest image.

Minimum image convention and the cut-off radius



- The cut-off radius has to be smaller than half the box length or the minimum image convention is violated!

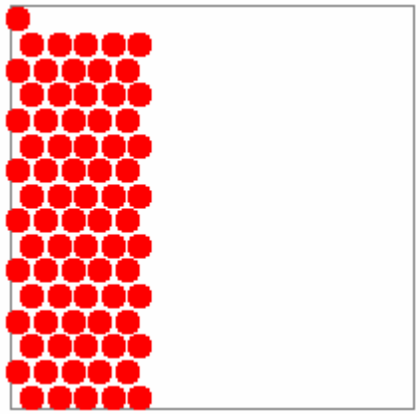
Setting up an MD simulation



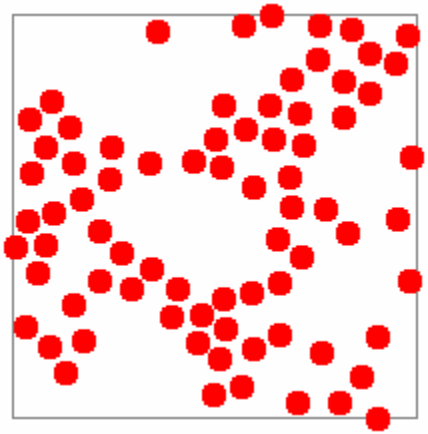
- Without any additional control measure, MD in microcanonical ensemble (NVE constant).
- A thermostat and a barostat can be used to run the simulation at constant T and P.

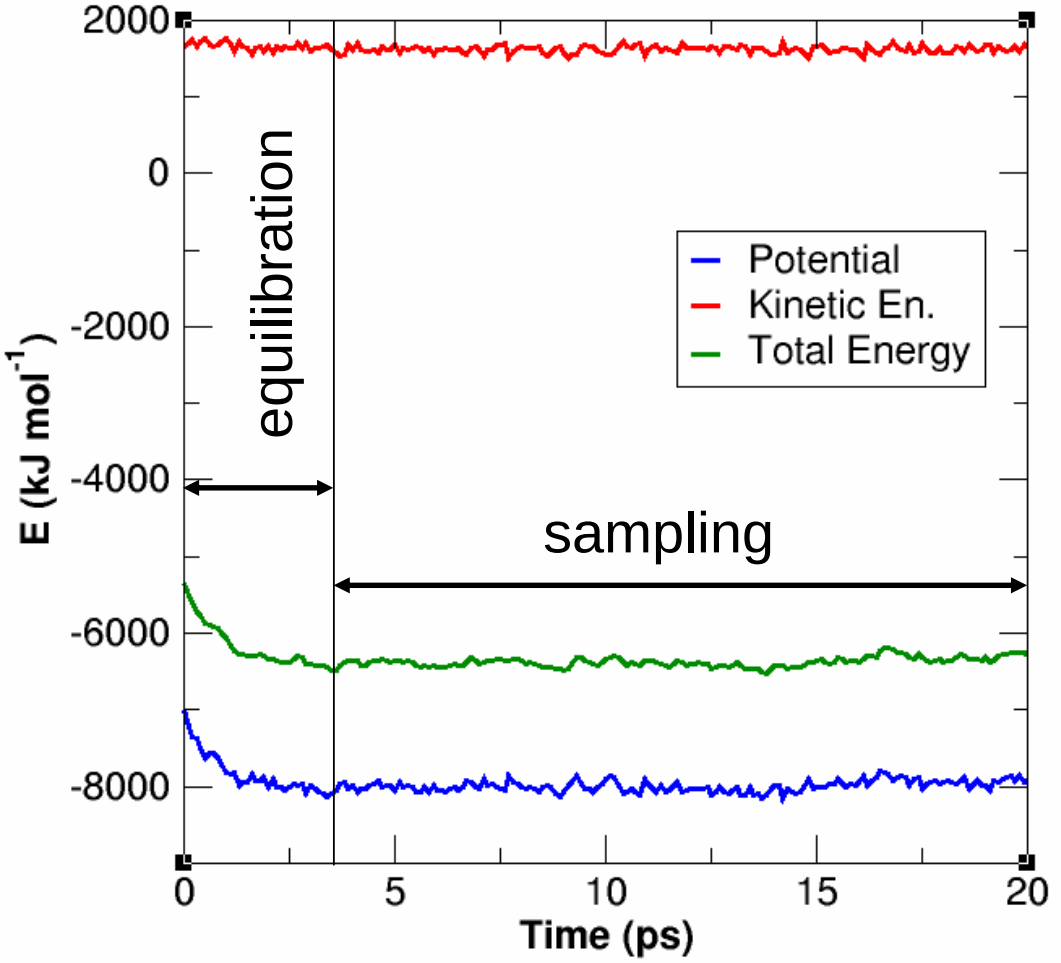
Sampling should only start once system has equilibrated

Initial configuration



An equilibrium configuration





Run MD

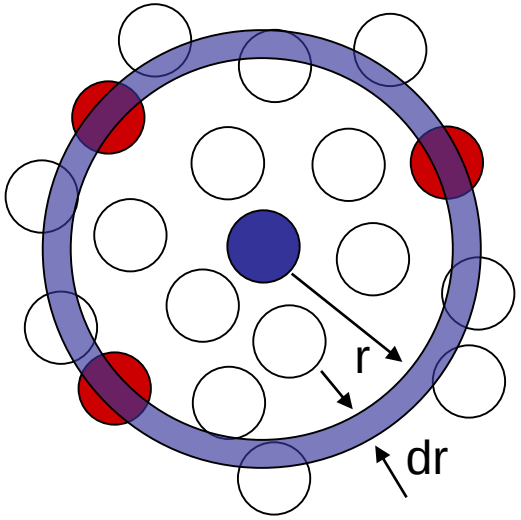
- http://rheneas.eng.buffalo.edu/wiki/LennardJones

Properties calculated:

- Velocity distribution (read more about Maxwell Boltzmann distribution on webpage)
- Kinetic and potential energy
- Radial distribution function
- Mean square displacement

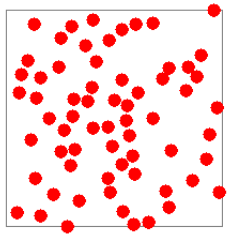
Have a play!

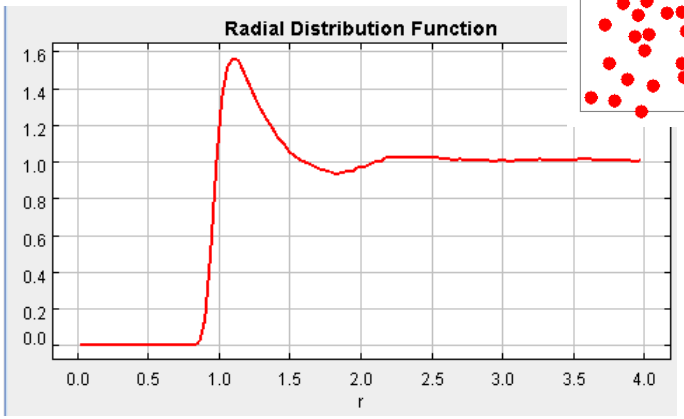
Sampling – radial distribution function



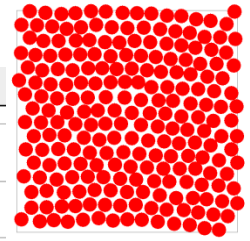
- Gives information about the structure
- “Given that I have one atom at some position, how many atoms can I expect to find at a distance r away from it?”
- the rdf can be measured experimentally, using neutron-scattering techniques

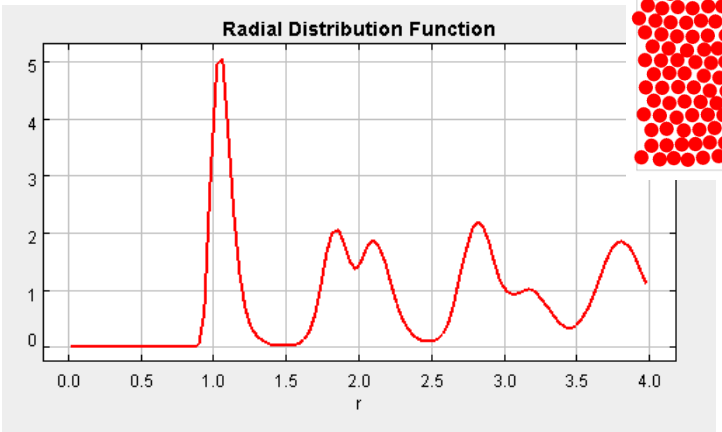
Gas like





Solid like





Sampling – self diffusion coefficient

- How far will a molecule travel in a given time interval?
- Mean square displacement:

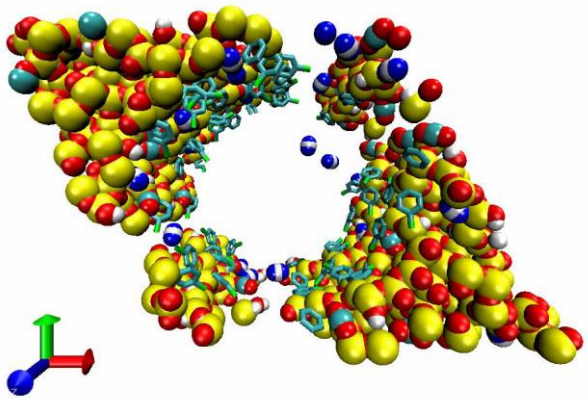
$$msd(t) = \left\langle \Delta r_i(t)^2 \right\rangle = \left\langle \left(r_i(t) - r_i(0)\right)^2 \right\rangle$$

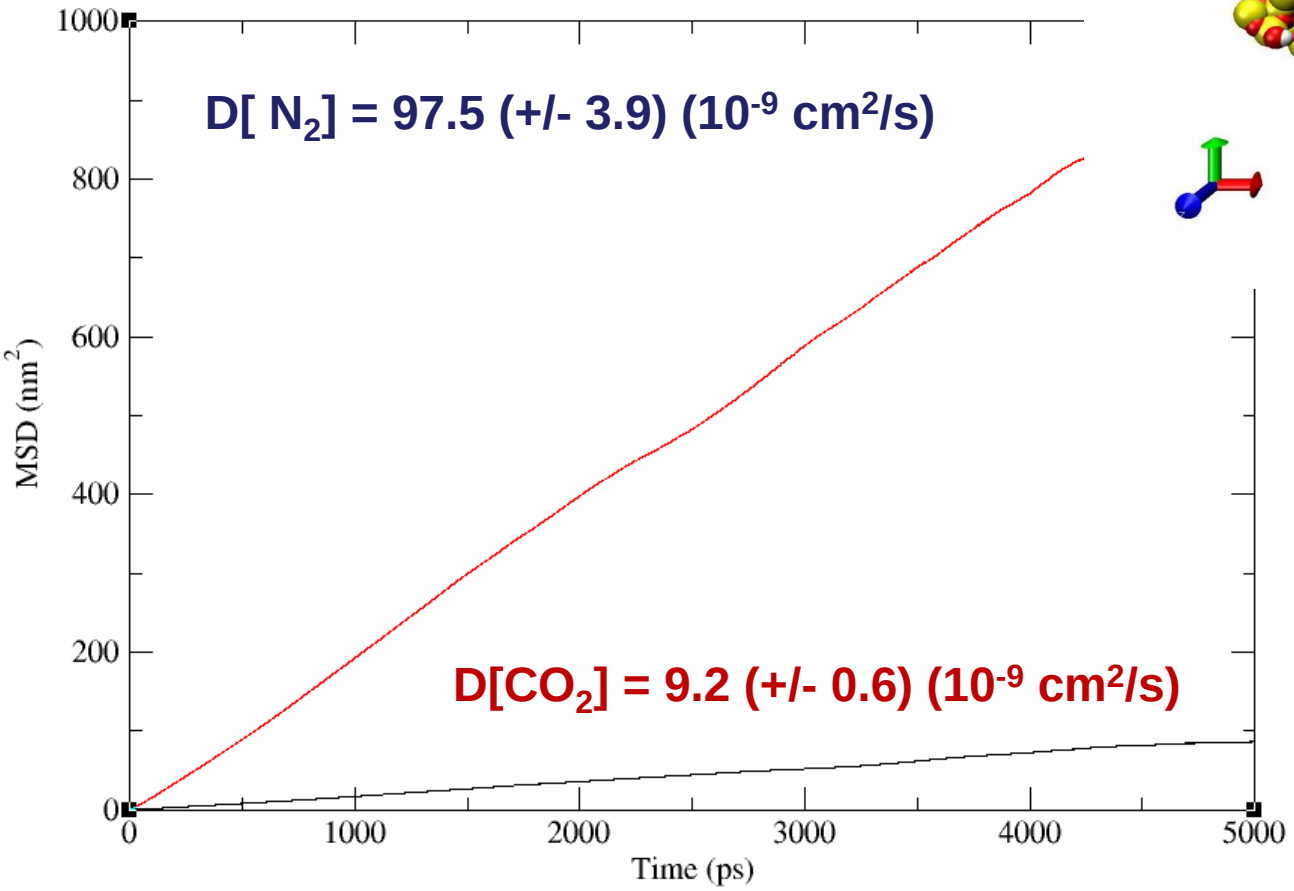
- Related through Einstein equation to macroscopic self-diffusion (= Brownian motion, no external driving force)

$$\frac{\partial \left\langle \mathbf{r}^2(t) \right\rangle}{\partial t} = 2d^{sys} D_{self}$$

- bulk systems: $d^{sys} = 3$, slit-like pores: $d^{sys} = 2$, cylindrical pores: $d^{sys} = 1$

Mean square displacement for flue gases in MCM-41





References

- D. Frenkel, B. Smit “Understanding Molecular Simulation” 2nd Editions, Academic Press, 2002
- J. M. Haile “Molecular Dynamics Simulation. Elementary Methods”, Wiley, 1992
- http://reaktiveplasmen.ruhr-uni-bochum.de/index.php?option=com_content&view=category&layout=blog&id=86&Itemid=157